Optimizing rotary processes in synthetic molecular motors

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Supporting Information

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SI Text

Experimental Part. ***Experiments 1–6.*** As in experiment 1, in experiment 2 pure stable isomer C (1) was simultaneously illuminated (λ = 365 nm) and heated (55.5 °C) to induce rotation of the motor molecules. The development of concentrations of all four isomers in course of time was monitored by ^{1}H NMR spectroscopy and is depicted in Fig. S1.

In experiment 3, pure B (1) was heated at 55.5 °C in the dark, which resulted in selective, complete conversion of B into C (k_{BC} = 6.5 × 10^{-5} s^{-1}, $\Delta G^{\ddagger}$ = 25.6 kcal mol^{-1}). The activation energy ($\Delta G^{\ddagger}$) was calculated with following equation: $\Delta G^{\ddagger} = -RT\ln(hk/k_BT)$. Experiment 4 was similar, starting with pure D (1) (k_{DA} = 10.2 × 10^{-5} s^{-1}, $\Delta G^{\ddagger}$ = 25.3 kcal mol^{-1}). Again, the activation energy ($\Delta G^{\ddagger}$) was calculated with following equation: $\Delta G^{\ddagger} = -RT\ln(hk/k_BT)$. The fact that both thermal conversions (experiments 3 and 4) are quantitative (full) is in line with previous energy calculations which revealed energy differences ($\Delta\Delta E$) of 4.65 kcal mol^{-1} for both pairs of stable versus unstable isomers ($\Delta E_D - \Delta E_A$ = +4.65 kcal mol^{-1} and $\Delta E_B - \Delta E_C$ = +4.65 kcal mol^{-1}) (1). Based on these numbers, the backward thermal rates, k_{CB} and k_{AD}, are negligible, because according to the Boltzmann distribution $k_{BC}/k_{CB} = k_{DA}/k_{AD}$ = 1.2 × 10^3 at 55.5 °C. Empirically established reaction rates k_{BC} and k_{DA} thus allowed calculation of k_{CB} and k_{AD} to be 5.4 × 10^{-8} s^{-1} and 8.5 × 10^{-8} s^{-1}, respectively.

Next, we performed experiment 5, during which we illuminated pure B with the proper wavelengths. This time, the temperature was kept low (5 °C) to exclude thermal conversion into C. This resulted in formation of A and D with rates of 2.1 × 10^{-5} s^{-1} (k_{BA}) and 0.7 × 10^{-5} s^{-1} (k_{BD}), respectively. Likewise, low-temperature irradiation of D (experiment 6) resulted in formation of B and C with rates of 1.1 × 10^{-5} s^{-1} (k_{DB}) and 3.2 × 10^{-5} s^{-1} (k_{DC}), respectively.

Experimental Section. ***General.*** The synthesis and purification of isomers A, B, C, and D (Scheme 1, main text) used in experiments 1–6 were described previously (1). Irradiation experiments were performed with a Spectroline ENB-280C/FE UV lamp at 365 nm. ^{1}H NMR spectra were obtained by using a Varian Mercury Plus operating at 399.93 MHz.

Experiment 1. an NMR tube (Pyrex, ∅ = 5 mm) was charged with a solution of racemic *trans*-1-[2-methoxy-thioxanthen-(9E)-ylidene]-2-methyl$_{axial}$-2,3-dihydro-1*H*-benzo[*f*]thiochromene (stable isomer A, 10 mg, 2.28 × 10^{-2} mmol) in toluene-d_8 (0.65 mL, c = 3.51 × 10^{-2} M). The NMR tube was placed in an oil bath at a static temperature of 55.5 °C and simultaneously illuminated with 365-nm light at exactly 15-cm distance from the lamp. At regular time intervals, the tube was removed from the bath and lamp and directly cooled to 0 °C to stop all isomerization processes. A ^{1}H NMR spectrum was recorded to monitor the fraction of isomers A, B, C, and D. Subsequently, the tube was replaced at the bath and lamp and isomerization processes were resumed. This procedure was repeated with time intervals ranging ≈5 × 10^2 s ($0 \le t \le 1.0 \times 10^4$ s) to ≈2.5 × 10^3 s ($1.0 \times 10^4 \le t \le 3.7 \times 10^4$ s) giving 32 data points and allowing a total irradiation and heating time of 3.7 × 10^4 s. The results are visualized in Fig. 1 in the main text (development of fractions A, B, C, and D in course of time) and given in Table S1 (fractions A, B, C, and D at equilibrium) and Table S2 (reaction constants).

Experiment 2. as described above for experiment 1. *Cis*-1-[2-methoxy-thioxanthen-(9E)-ylidene]-2-methyl$_{axial}$-2,3-dihydro-1*H*-benzo[*f*]thiochromene (stable isomer C). Total irradiation and heating time: of 4.15 × 10^4 s. Thirty-four data points. The results are visualized in Fig. S1 (development of fractions A, B, C, and D in course of time) and given in Table S1 (fractions A, B, C, and D at equilibrium) and Table S2 (reaction constants).

Experiment 3. an NMR tube (Pyrex, ∅ = 5 mm) was charged with a solution of racemic *cis*-1-[2-methoxy-thioxanthen-(9E)-ylidene]-2-methyl$_{equatorial}$-2,3-dihydro-1*H*-benzo[*f*]thiochromene (unstable isomer B, 10 mg, 2.28 × 10^{-2} mmol) in toluene-d_8 (0.65 mL, c = 3.51 × 10^{-2} M). The tube was heated at 55.5 °C under exclusion of light and conversion into stable isomer C (formation of isomers A and/or D was not observed) was monitored with ^{1}H NMR spectroscopy at regular time intervals. A Gibbs energy of activation $(\Delta G^{\ddagger})_{BC}$ of 25.6 kcal mol^{-1} was established. From this value the activation energy for the backward reaction was calculated to be $(\Delta G^{\ddagger})_{CB}$ = 30.3 kcal mol^{-1}.

Experiment 4. As described above for experiment 3. Only conversion of *trans*-1-[2-methoxy-thioxanthen-(9E)-ylidene]-2-methyl$_{equatorial}$-2,3-dihydro-1*H*-benzo[*f*]thiochromene (unstable isomer D) into stable A was observed. $(\Delta G^{\ddagger})_{DA}$ = 25.3 kcal mol^{-1}. $(\Delta G^{\ddagger})_{AD}$ = 30.0 kcal mol^{-1}.

Experiment 5. an NMR tube (Pyrex, ∅ = 5 mm) was charged with a solution of racemic *cis*-1-[2-methoxy-thioxanthen-(9E)-ylidene]-2-methyl$_{equatorial}$-2,3-dihydro-1*H*-benzo[*f*]thiochromene (unstable isomer B, 10 mg, 2.28 × 10^{-2} mmol) in toluene-d_8 (0.65 mL, c = 3.51 × 10^{-2} M). The NMR tube was placed in an oil bath at a temperature of <5 °C and simultaneously illuminated with 365-nm light at exactly 15-cm distance from the lamp. At regular time intervals the tube was removed from the bath and lamp and kept cooled to 0 °C to stop all isomerization processes. A ^{1}H NMR spectrum was recorded to monitor the fractions of isomers A, B, C, and D. Subsequently, the tube was replaced at the bath and lamp and isomerization processes were resumed. This procedure was repeated giving 20 data points. The results are given in Table S2 (reaction constants).

Experiment 6. As for experiment 5. *Trans*-1-[2-methoxy-thioxanthen-(9E)-ylidene]-2-methyl$_{equatorial}$-2,3-dihydro-1*H*-benzo[*f*]thiochromene (unstable isomer D). The results are given in Table S2 (reaction constants).

Notes to the Theory. ***Calculating the evolution of the molecular fractions.*** To solve Eq. **1**, we first take its transpose to obtain $\mathbf{X}^T(t + \Delta t) = \mathbf{P_0}^T\mathbf{X}^T(t)$, where $\mathbf{X}^T$ is now a column vector. This is rewritten as $d\mathbf{X}^T/dt = \mathbf{K}\,\mathbf{X}^T(t)$, replacing Δt by an infinitesimal interval dt, and defining the 4 × 4 matrix $\mathbf{K} = (\mathbf{P_0}^T - \mathbf{I})/dt$, where $\mathbf{I}$ is the 4 × 4 identity matrix. This equation has the standard solution $\mathbf{X}^T(t) = \mathrm{Exp}(t\mathbf{K})\ \mathbf{X}^T(t = 0)$, where Exp denotes the matrix exponent. The vector $\mathbf{X}^T(t = 0)$ describes the initial state of the system, i.e., $\mathbf{X}^T(t = 0) = (1, 0, 0, 0)^T$ and $\mathbf{X}^T(t = 0) = (0, 0, 1, 0)^T$ for experiments 1 and 2, respectively.

Prefactor $c_K(\Phi)$. Here, we consider the isomer-specific prefactor $c_K(\Phi)$ in more detail. Suppose we started with material A only, like in experiment 1, and equilibrium is reached. Then, all molecules that are in shape A, have exactly made an integer number n of full rotations, i.e., $4n$ quarter rotations (our units of choice). Thus for each time t, we have $\Phi_t = 4n$, $n \in \mathbf{Z}$, for these molecules. Molecules in shape B, C and D have $\Phi_t = 4n + 1$, $\Phi_t = 4n + 2$ and $\Phi_t = 4n + 3$, respectively. Equivalently, one can state that the probability to find an isomer A that has $\Phi_t = 4n + 1$ must equal zero; such states are not allowed. Only if a value for Φ is "allowed" for a certain isomer K, we have a nonzero prefactor,

$c_K(\Phi$ allowed) $\equiv a_K$. For example, $c_B(\Phi = 5) = a_B \neq 0$, but $c_B(\Phi = 6) = 0$. To find a_K, we note that the sum of all fractions $\mu_t^{(K)}(\Phi)$ must, at any time t, equal the total fraction of isomer K. This equals the equilibrium concentration w_K for large t. For example, the total fraction of molecules that completed $4n + 1$ rotations at equilibrium must equal w_B, because only isomers in state B can have $\Phi_t = 4n + 1$. To quantify a_K, we thus sum $\mu_t^{(K)}(\Phi)$ over all Φ. For large t, this sum can be written as an integral, with a value $\frac{1}{4}a_K$. Hence, we have $a_K = 4w_K$. Note that for more general initial conditions, e.g., if we start with 40% A and 60% C, the $c_K(\Phi)$-values can be found by the superposition principle.

1. Koumura N, Geertsema EM, van Gelder MB, Meetsma A, Feringa BL (2002) Second generation light-driven molecular motors. Unidirectional rotation controlled by a single stereogenic center with near-perfect photoequilibria and acceleration of the speed of rotation by structural modification. *J Am Chem Soc* 124:5037–5051.

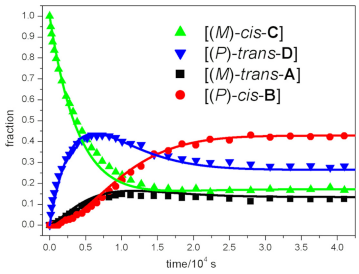

Fig. S1. Fraction development in course of time during experiment 2.

Table S1. Equilibrium fractions w_K of motor isomers A, B, C, and D during simultaneous input of photons (365 nm) and heat (55.5 °C), for experiments 1 and 2

Isomer	Empirical data		Calculated fraction at equilibrium
	Fraction at $t = 0$	Fraction at equilibrium	
Experiment1			
A	1.00	0.12	0.13
B	0	0.43	0.43
C	0	0.17	0.17
D	0	0.28	0.27
Experiment 2			
A	0	0.12	0.13
B	0	0.43	0.43
C	1.00	0.17	0.17
D	0	0.28	0.27

The rightmost column shows equilibrium fractions, calculated by using Eqs. **1**–**3**, main text, and Table S2.

Table S2. Empirically determined reaction rates

Experiment	Starting material	Energy input	Reaction constant	Reaction rate ($k/10^{-5}$ s^{-1})	Reaction constant	Reaction rate ($k/10^{-5}$ s^{-1})	Reaction constant	Reaction rate ($k/10^{-5}$ s^{-1})
1 (Fig 1)	A	$h\nu$ and Δ	k_{AB}	27.4	k_{AC}	1.4	k_{AD}	8.5×10^{-3}*
2 (Fig S1)	C	$h\nu$ and Δ	k_{CD}	20.6	k_{CA}	1.6	k_{CB}	5.4×10^{-3}†
3	B	Δ	k_{BC}	6.5	k_{BD}	n.o.	k_{BA}	n.o.
4	D	Δ	k_{DA}	10.2	k_{DB}	n.o.	k_{DC}	n.o.
5	B	$h\nu$	k_{BC}	n.o.	k_{BD}	0.7	k_{BA}	2.1
6	D	$h\nu$	k_{DA}	n.o.	k_{DB}	1.1	k_{DC}	3.2

n.o., not observed. Illumination and heating (55.5 °C) are indicated by hν and Δ, respectively.
*Calculated value from k_{DA} (experiment 4) (1).
†Calculated value from k_{BC} (experiment 3) (1).

Other Supporting Information Files

SI Appendix (PDF)
Other S1 (TXT)
Other S2 (TXT)